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A Study of the Blistering of Metal Surfaces
By Solar System Ions

Prepared by:

James A. Cooley
James A. Cooley
Staff Scientist

Approved by:

William R. Holland
William R. Holland, Chief
Environmental Physics Section

Approved by:

D. G. Crews
D. G. Crews
Manager of Engineering

AVCO ELECTRONICS DIVISION
TULSA OPERATION

ABSTRACT

An electron microscope study of proton irradiated sample surfaces was conducted. Pitting of surface oxides may result from blistering followed by exfoliation. Orientation dependence of aluminum blistering is reported. A mass spectrometric study of hydrogen evolution from irradiated aluminum was conducted. No correlation was found between gas evolution and blistering.

FOREWORD

This report was prepared by the Tulsa Operation of the Avco Electronics Division under Contract NASw-1431 issued by the Office of Advanced Research and Development of the National Aeronautics and Space Administration. The program is monitored by Dr. R. R. Nash of NASA/Headquarters and D. L. Anderson of NASA/Ames Research Center.

This report covers work performed from 14 June 1966 through 14 September 1966.

I. INTRODUCTION

Major laboratory effort during the first quarter was devoted to an electron microscope study of irradiated sample surfaces previously examined under the optical microscope. Replicas of the sample surfaces were examined under the electron microscope. A portion of the period was devoted to development of the procedures for preparing surfaces.

A total of seven samples were irradiated during the period. Four of these were pure aluminum and the other three were pure gold.

A mass spectrometer study of hydrogen evolution from proton bombarded aluminum samples was conducted during the period. Results indicated no correlation between hydrogen evolution and the appearance of blisters.

II. ELECTRON MICROSCOPE STUDIES

A. Replication Techniques

To observe the surface effects of proton irradiation on the aluminum surfaces, two methods of replication were evaluated. Both aluminum oxide and plastic replica techniques were used, but the plastic replication method proved much more versatile because the aluminum oxide technique required use of mercuric chloride which destroyed the sample. With the plastic replication technique, it was possible to prepare several replicas from a single sample.

A single stage replication technique using a one percent solution of Formvar in dioxane gave best results. Formvar was chosen because of its strength, high resolution capabilities, and resistance to heat effects. The negative replicas prepared in this manner were viewed under the electron microscope after shadowing with either chromium or gold. The first samples prepared were shadowed with chromium but later procedures utilized gold because its greater density gave better contrast and resolution.

The angle of shadowing proved to be a critical factor in reproducing the surface characteristics of the samples. When the angle of shadowing is small, a great deal of fine detail could be resolved while the larger imperfections appeared distorted. An increase in the angle of shadowing improved the resolution of large structure but resulted in a loss of fine detail. To counteract these opposite effects, a technique in which samples were shadowed at two angles was employed. The best results were obtained with angles of approximately 20° and 8° .

B. Discussion of Studies

Examples of structures observed under the electron microscope are shown in Figures 1 and 2. Figure 1 is an electronmicrograph at a magnification of 14,000X of a sample irradiated with 100 Kev protons. The micrograph shows the edge of the irradiated area of a pitted and blistered specimen. This micrograph was taken on the sample after irradiation and annealing but prior to stripping of the oxide. In addition to the pitting and blistering

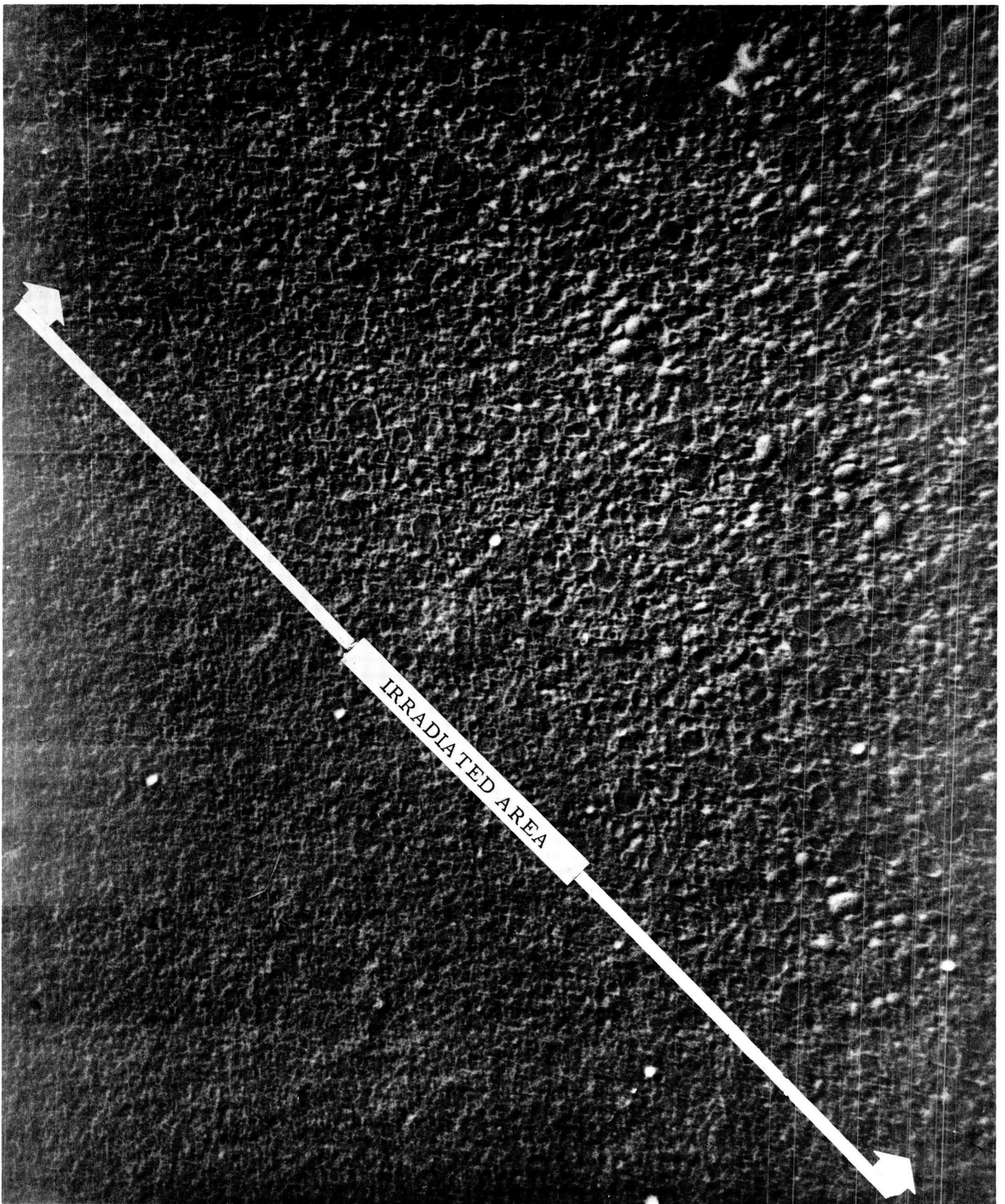


Figure 1 - Magnification 14,000X. Electron Micrograph.
High Purity Aluminum - Annealed. 100 Kev Protons.
Edge of Irradiated Area of Pitted and Blistered
Specimen.

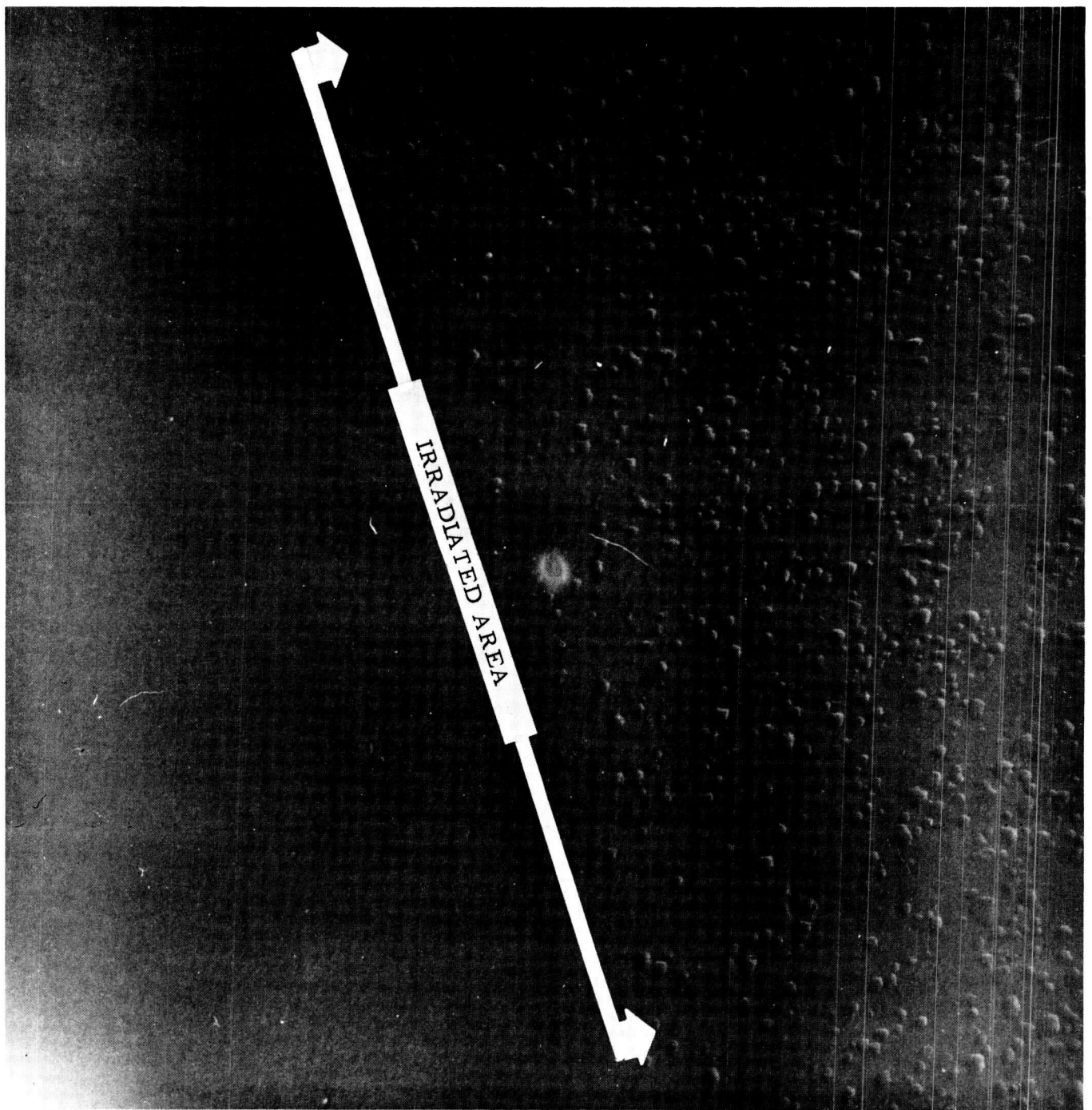


Figure 2 - Magnification 11,000X.
Electron Micrograph of High Purity
Aluminum Irradiated with 100 Kev
Protons. Annealed Sample with Oxide
Chemically Stripped.

in the irradiated area, the micrograph shows some of the texture of the surface oxide. Figure 2 is an electronmicrograph of the same sample after the oxide has been stripped by techniques described earlier*. It can be seen that the removal of the oxide effectively removes all evidences of pitting and greatly reduces the apparent rough texture of the surface, but does not eliminate the blisters.

Evidence that blistering and exfoliation of the surface oxide may appear as pitting is provided in the electronmicrograph, Figure 3. This sample irradiated with 100 kev protons was examined in the as-irradiated condition. This sample shows evidence of blister formation at the metal oxide interface. Removal, or exfoliation, of the oxide may be what is observed as pits at lower magnifications.

Evidence for collapse of blisters is presented in Figure 4. This sample was irradiated at 100 kev, subsequently annealed, and the oxide was chemically removed. Note the presence of blisters which have collapsed. There was no evidence of pitting here since such effects have been removed by stripping of the oxide.

Studies of the development of pitting and blistering using the oxide stripping technique were continued during the first quarter. Examples of the results which have been obtained using this technique of analysis are shown in Figures 5, 6, and 7. Figure 5 shows the intersection of three grains of a polycrystalline sample irradiated with 100 kev protons. This photomicrograph was obtained under bright field illumination at a magnification of 1,500X. The pitting of the oxide is the most prominent feature here. Figure 6 is a photograph of the same area shown in Figure 5 after the oxide film has been removed by chemical stripping. Figure 7 is a photograph of the same area after the sample shown in Figures 5 and 6 had been annealed. This photomicrograph shows the development of blisters. The sequence of figures, 5, 6, and 7, demonstrates conclusively that the pitting observed is associated with the oxide layer, and that blistering is associated with swelling of the matrix material.

* "A Study of Blistering of Metal Surfaces by Solar System Ions," Final Report Contract NASw-1203, Avco Document TR 66-G-106-F, August 1966.

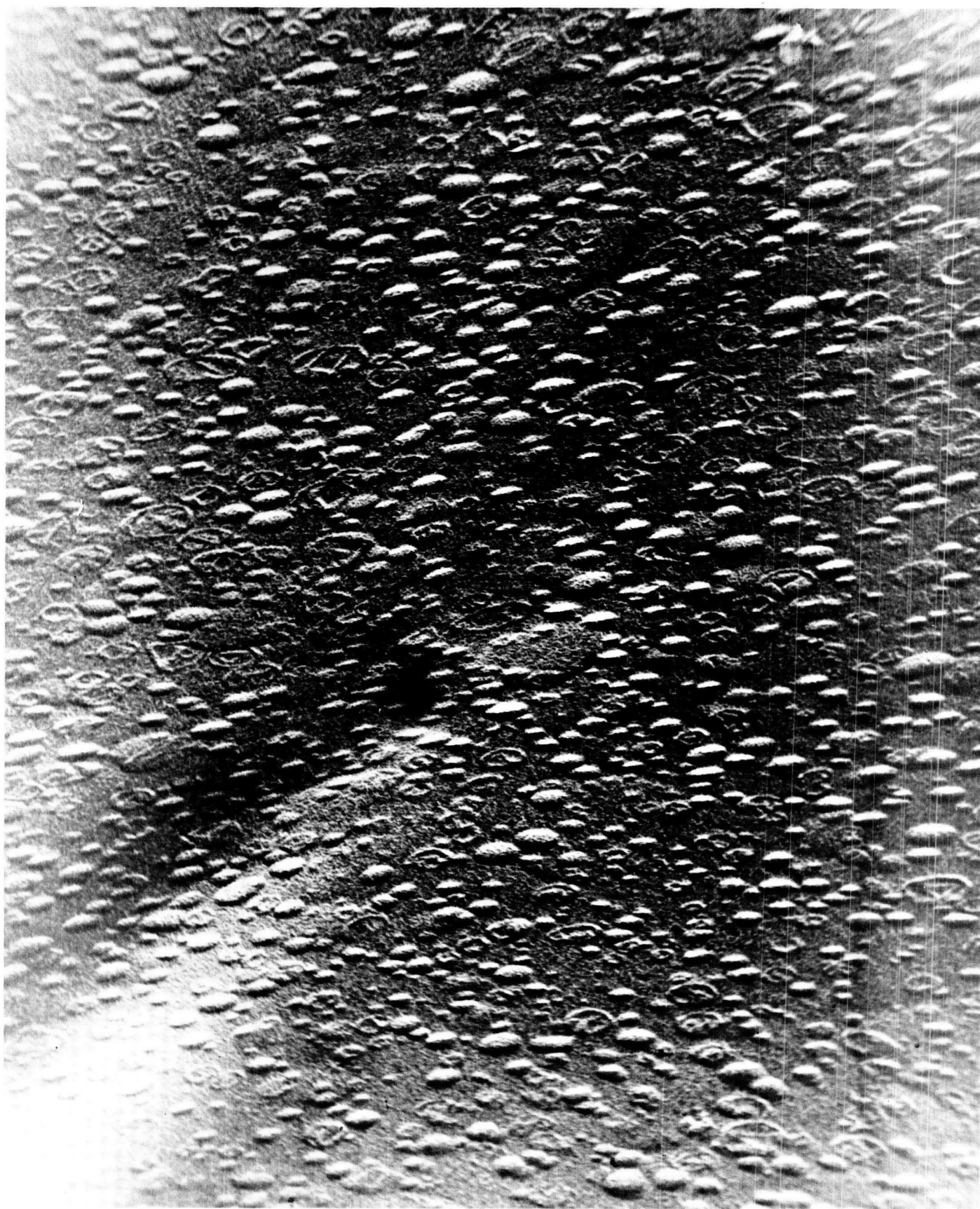


Figure 4 - Magnification 14,000X. Electron Micrograph.
High Purity Aluminum. Annealed with Oxide
Chemically Removed. 50 Kev Protons. Elongated
Blisters Some of which have Collapsed.

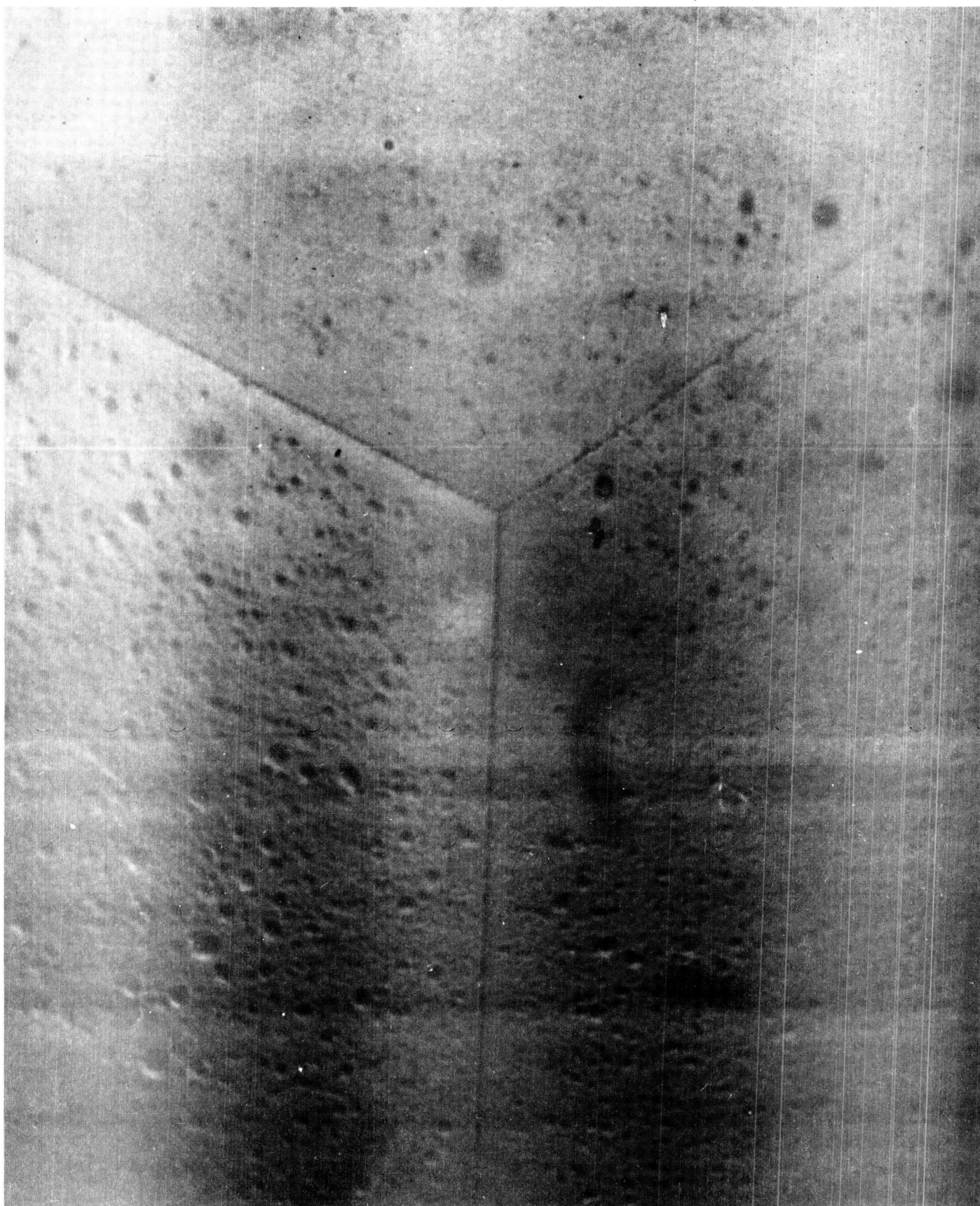


Figure 5 - Magnification 1500X. Enlarged 2.3X. Numerical
Aperature 1.4. Bright Field Illumination. High Purity
Aluminum - As-Irradiated Condition. 100 Kev Protons.
Pitting of Oxide on Polycrystalline Specimen.

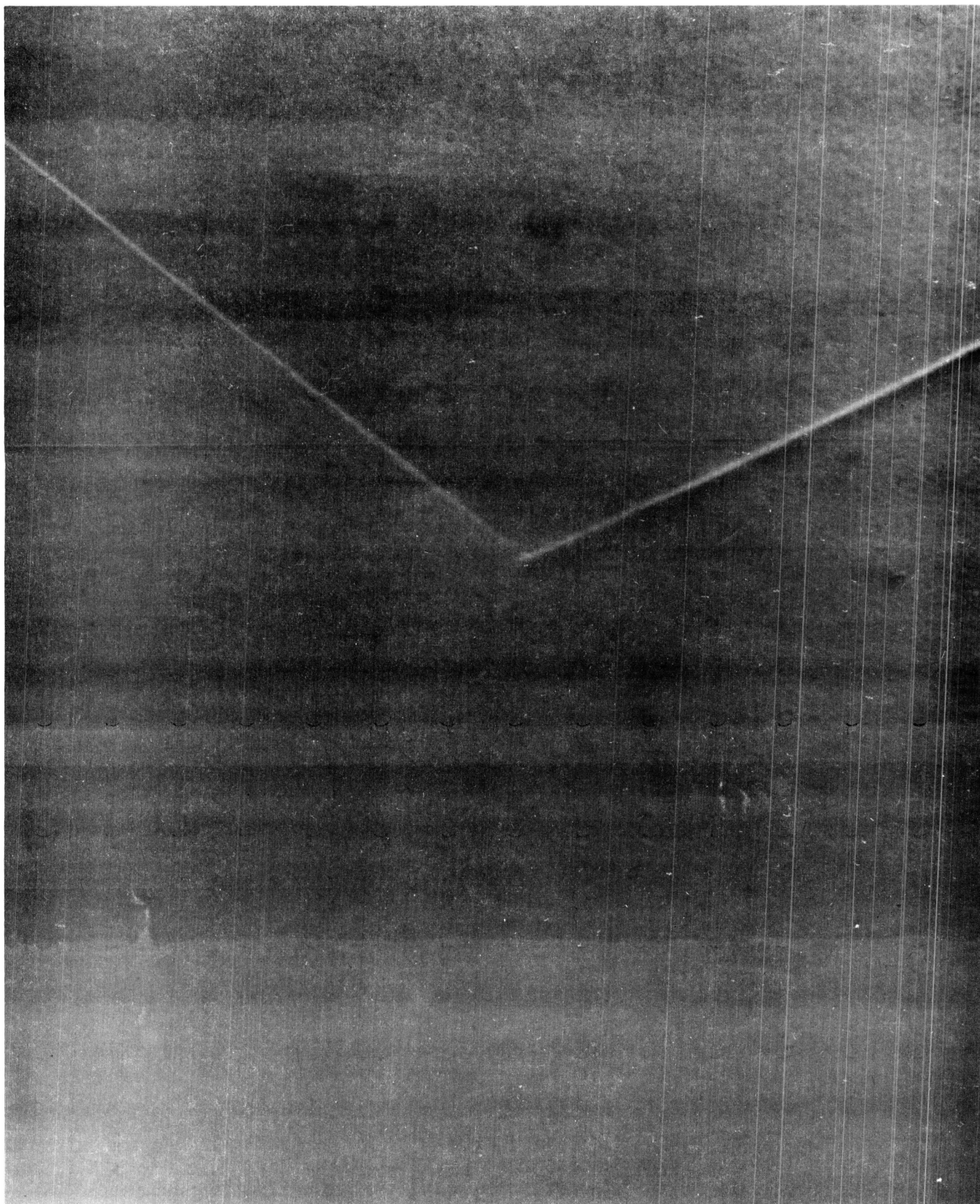


Figure 6 - Magnification 1500X. Enlarged 2.3X. Numerical Aperture 1.4. Bright Field Illumination. High Purity Aluminum - As-Irradiated. 100 Kev Protons. Irradiated Polycrystalline Specimen with Oxide Chemically Removed.

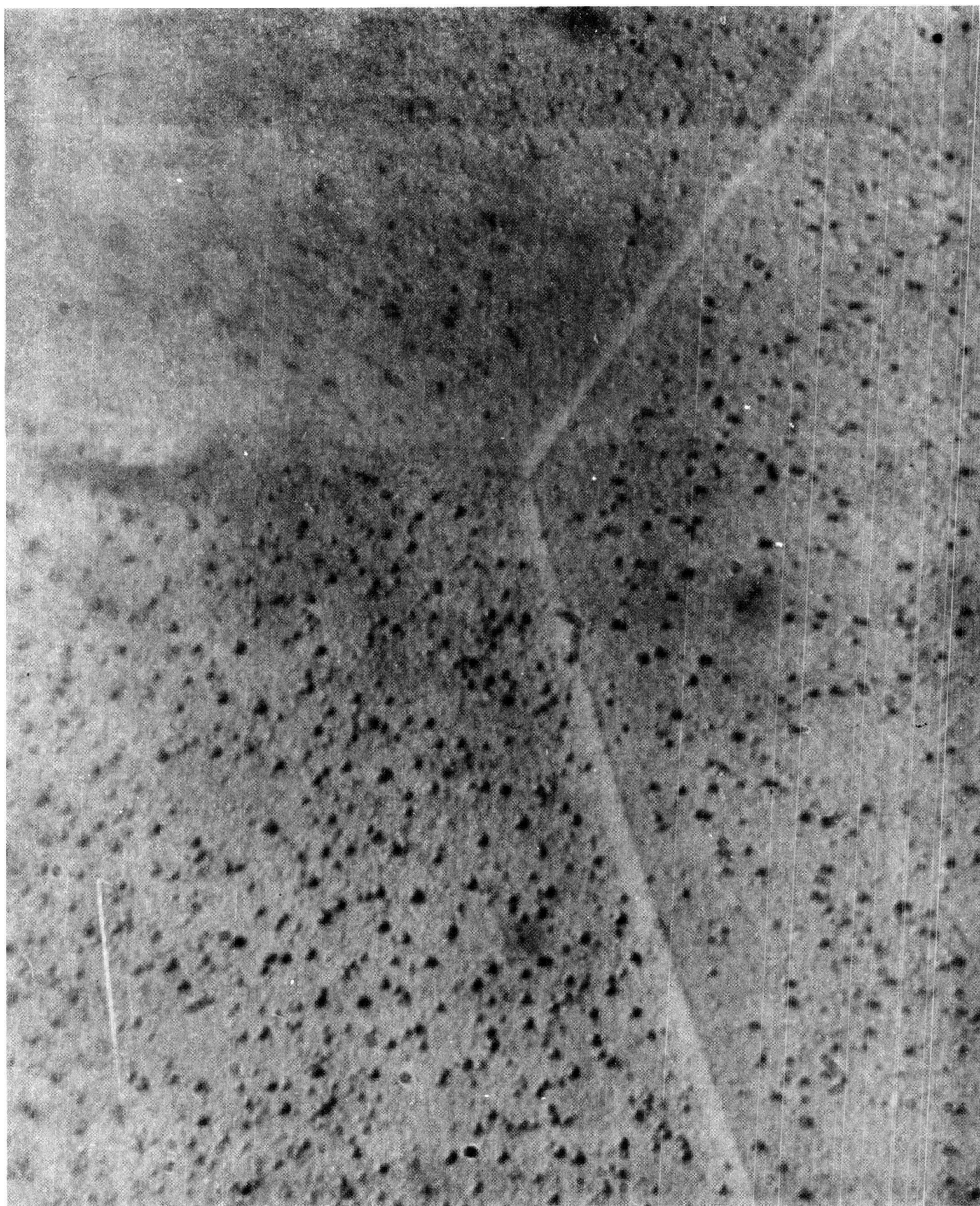
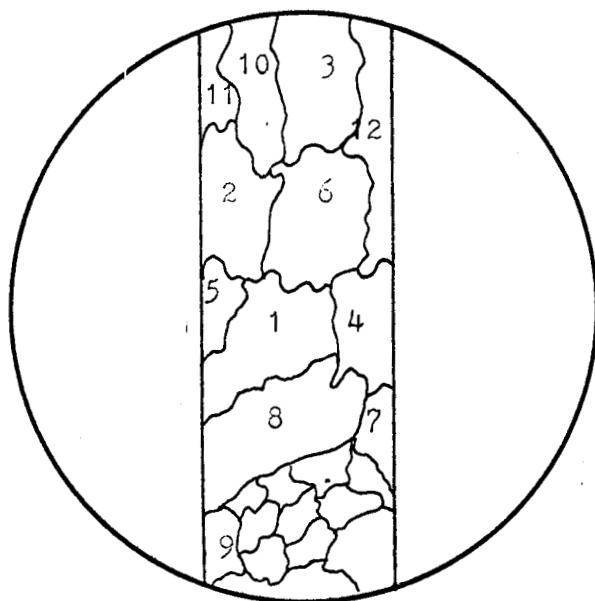


Figure 7 - Magnification 1500X. Enlarged 2.3X. Numerical Aperature 1.4. Bright Field Illumination. High Purity Aluminum - Annealed. 100 Kev Protons. Irradiated and Annealed Polycrystalline Specimen with Oxide Chemically Removed.

III. ORIENTATION DEPENDENCE OF BLISTER FORMATION

A study of the orientation dependence of blister formation, similar to that reported* for pit formation, was carried out. The results are presented graphically in Figures 8, 9, and 10. The samples employed in this study were the same samples used in the study of pit formation except that the samples were stripped of their oxide film and annealed to develop blisters. Identification and orientation of grains within the irradiated area, classified on the basis of degree of blistering, are shown in Figure 8 for a representative sample. The orientation of grains based on a classification of light, medium, and heavy blistering for a total of eight samples is shown in Figure 9. It can be seen that light blistering occurs near the 111 pole and that medium and heavy blistering occur with about equal frequency for other orientations. There is some suggestion that medium blistering may preferentially occur at the 100 pole. A composite diagram showing the probable orientations of light, medium, and heavy blistering represented on a stereographic triangle is represented in Figure 10. It appears that the orientation dependences of pitting and blistering are similar.

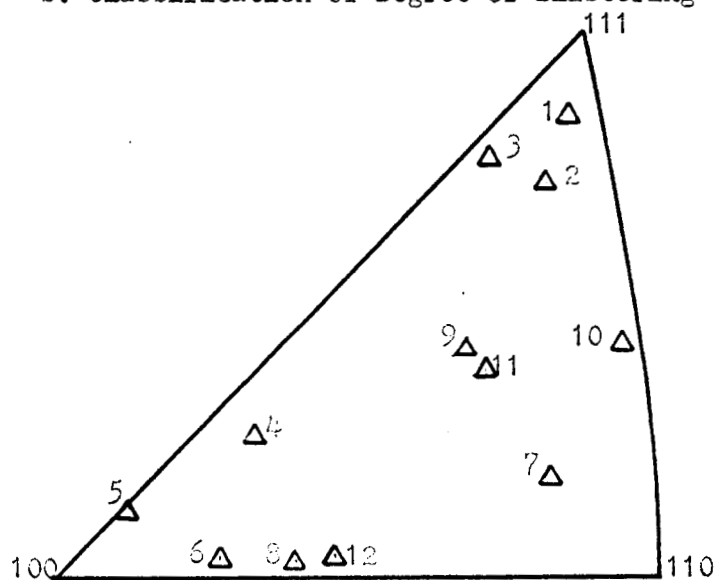
*"A Study of Blistering of Metal Surfaces by Solar System Ions," Final Report Contract NASw-1203, Avco Document TR 66-G-106-F, August 1966.



a. Representation of Irradiated Grains

Light	Medium	Medium to Heavy
1	5	4 10
2	6	7 11
3		8 12
		9

b. Classification of Degree of Blistering



c. Grain Orientations Plotted on Stereographic Triangle

Figure 8 -- Identification, Classification, and Orientation of Grains within Irradiated Area. Classification is based upon degree of blistering.

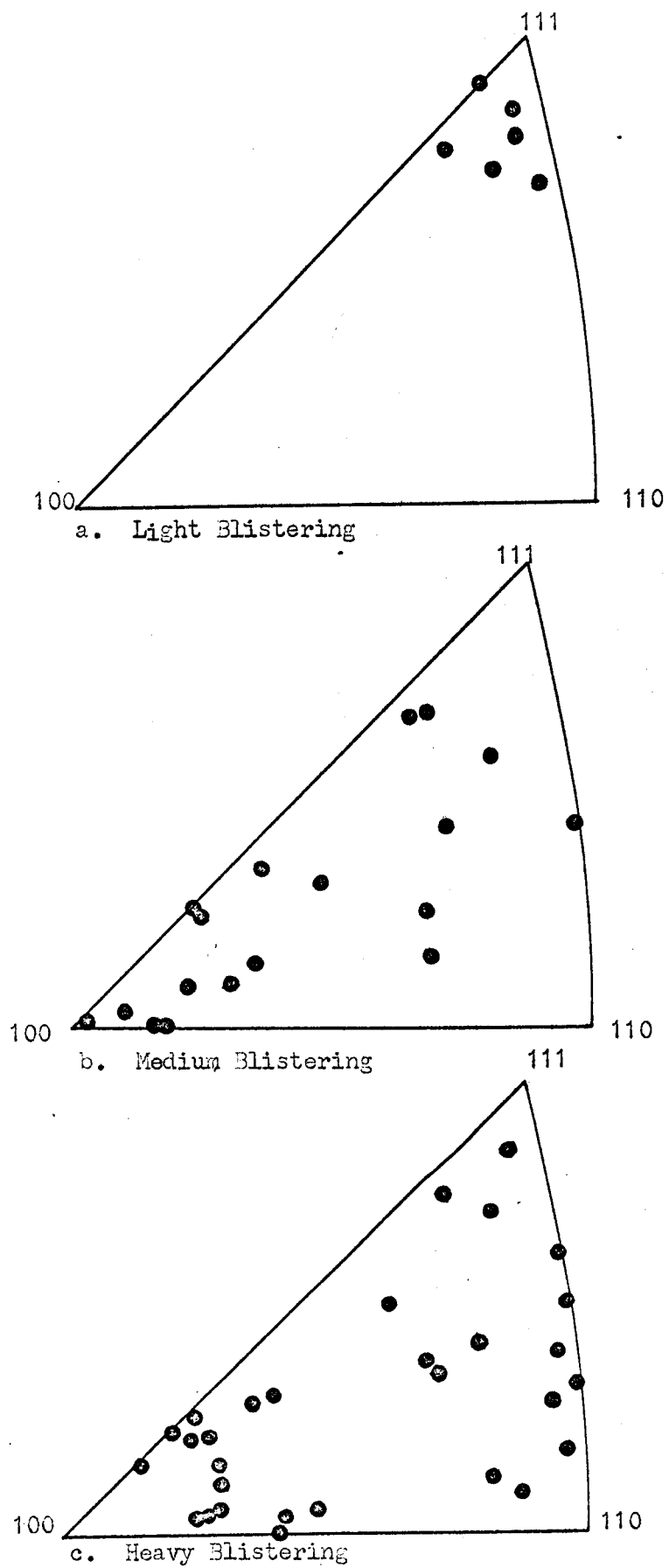


Figure 9-- Orientation of Grains Based upon Classification According to Degree of Blistering.

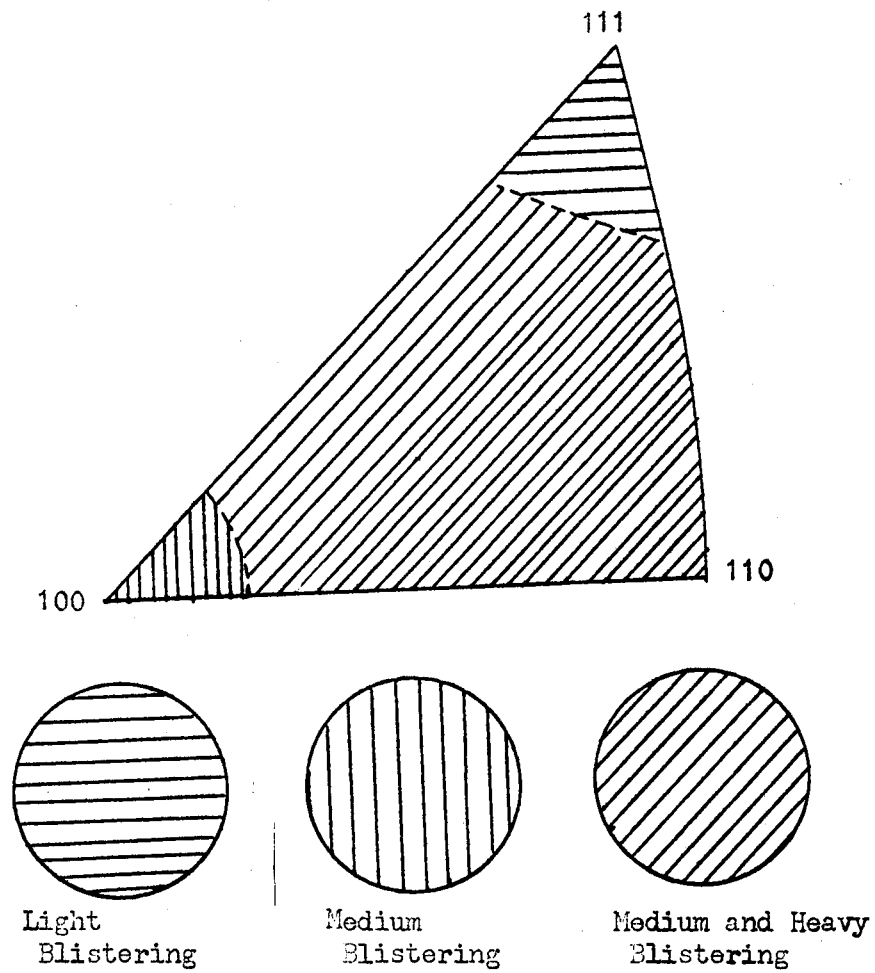


Figure 10-- Composite Diagram Showing Orientations of Light, Medium, and Heavy Blistering Represented as Areas on Stereographic Triangle.

IV. SAMPLE IRRADIATIONS

Tabulated below are the sample irradiations conducted during the quarter. All samples were maintained at 15°C during irradiation.

Sample No.	Sample Material	Protons		
		Kev	$p/cm^2/sec \times 10^{-12}$	$p/cm^2 \times 10^{-17}$
81	Pure Al	100	11	1.0
82	Pure Al	100	11	1.0
83	Pure Al	100	11	1.0
84	Pure Al	100	11	1.0
85	Pure Au	100	11	1.0
86	Pure Au	100	11	1.0
87	Pure Au	50	6.4	1.0

V. A MASS SPECTROMETRIC STUDY OF HYDROGEN EVOLUTION FROM PROTON BOMBARDED ALUMINUM

This study utilized a mass spectrometer to monitor the hydrogen evolution from proton bombarded aluminum subjected to various heating schedules. The objective of the study was to correlate the loss of hydrogen from the bombarded samples with the phenomenon known as "proton blistering". It was felt that this type of information would be valuable in helping to establish the blistering mechanism or mechanisms. The work reported here was done by Mr. James Wolfe at the Graduate Center for Materials Research of the University of Missouri at Rolla, Missouri.

A. Previous Work

Only one study has been found in the literature that is similar to the work presented in this report. Kaminsky* used a mass spectrometer to determine the species leaving the surface of copper and silver single crystals during bombardment by protons, deuterons, and helium ions in the energy range 0.1 to 4.0 MeV. Although this investigation was primarily a sputtering study, it was observed that the incident particles formed gas bubbles in the surface and these bubbles in turn exploded to re-emit the incident species. The authors were able to correlate apparent blister density with gas bursts observed by the mass spectrometer.

B. Experimental Techniques

The vacuum system used in this investigation consists of an all metal chamber pumped by a 500 L/sec ion pump. The system is capable of routinely obtaining vacuums in the 10^{-10} torr region. The samples were heated by resistance heating in a small tantalum wound alumina tube. The heating geometry is shown in Figure 11. The temperature was monitored by means of an iron-constantan thermocouple spotwelded on the un-irradiated end of the sample. The constituent gases in the vacuum chamber and the hydrogen liberation during annealing were followed with a General Electric Monopole Mass Spectrometer. The location of the mass spectrometer in relation to the sample is shown in Figure 12.

* M. Kaminsky, Adv. in Mass Spec., Vol. 3, 1964.

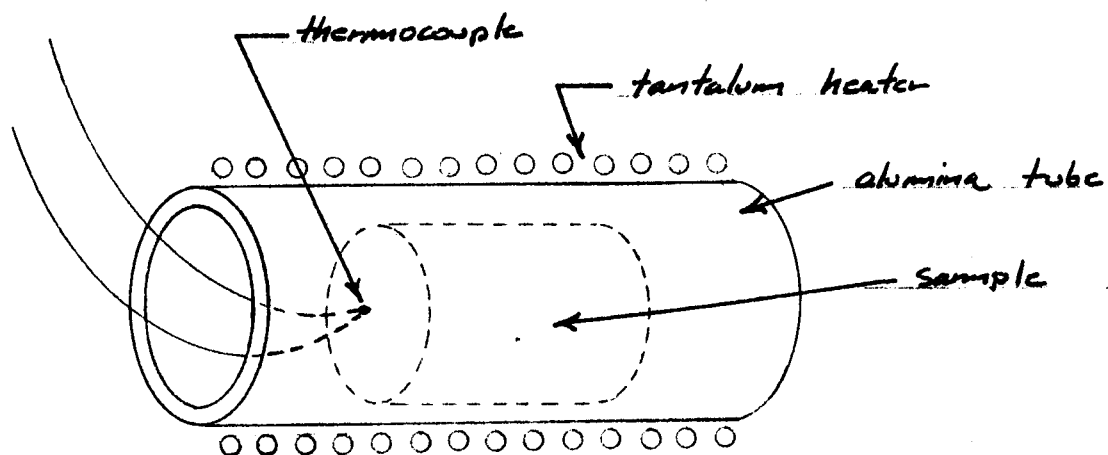


Figure 11 --- Heater and Sample Geometry

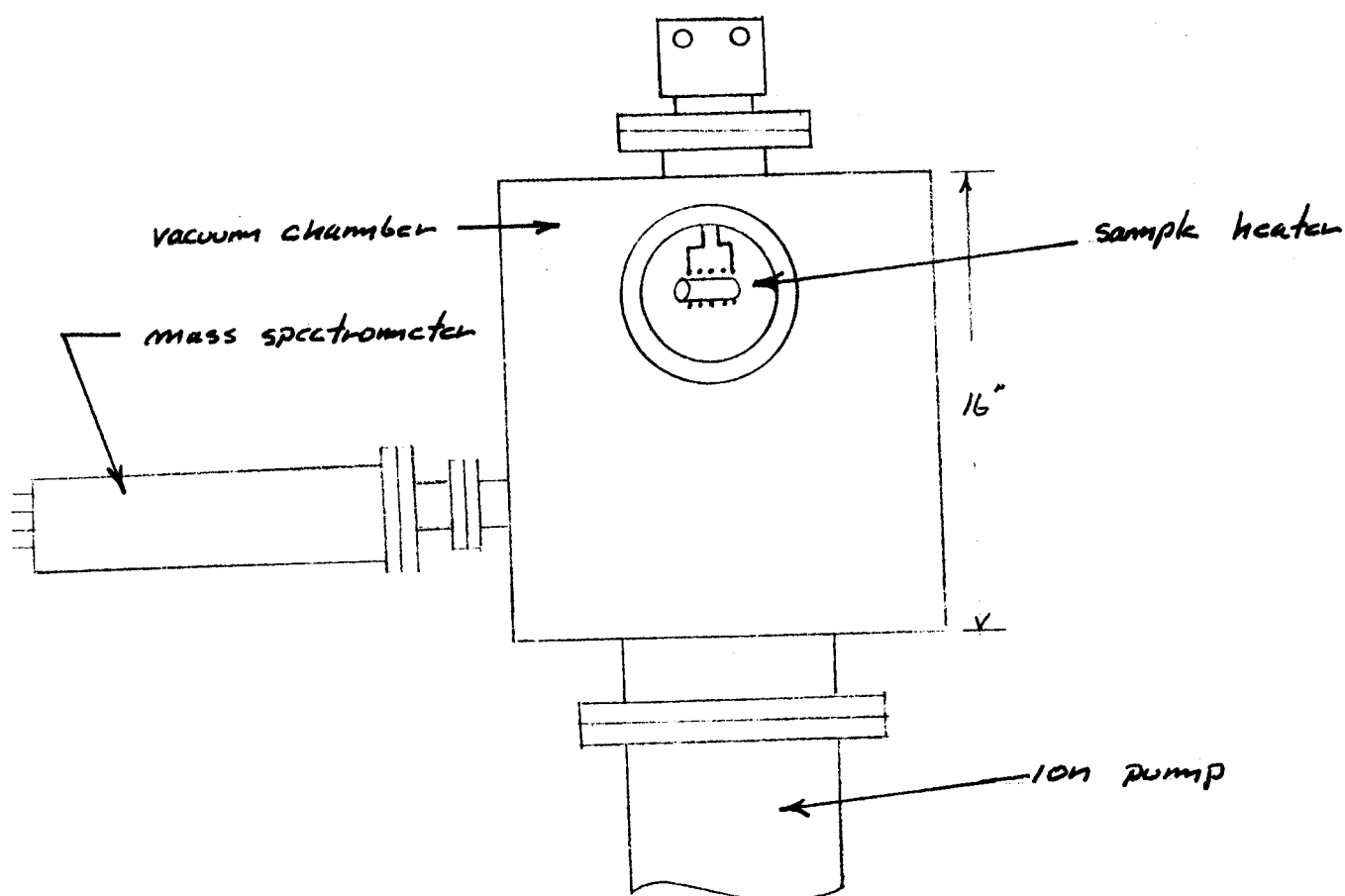


Figure 12 --- Mass Spectrometer Location

A typical experiment is as follows. The system is pumped down to 10^{-9} torr, empty, and the specimen holder is outgassed at 500°C for approximately 30 minutes. The entire system is then baked out at 250°C for approximately 10 hours, with a resulting vacuum in the low 10^{-10} torr or high 10^{-11} torr region. The system is then released to atmosphere under dry nitrogen, the sample inserted, and the system immediately pumped down with a resulting overnight pressure of approximately 5×10^{-10} torr obtained. A check of the constituent gases in the chamber is made and then the ion pump is then turned off and the hydrogen (H_2) peak is monitored to check for any anomalous hydrogen outgassing. The ion pump is then turned back on and the sample is brought up to the appropriate annealing temperature, while the mass spectrometer is simultaneously monitoring the H_2 evolution.

C. Materials

The material used in this investigation was single crystal aluminum which in sample form consisted of small cylinders approximately one centimeter in diameter and one and one-half centimeters in length. The samples were received from Dr. Raymond Daniels of the University of Oklahoma. The irradiated surfaces were prepared by Mr. Leonard Milacek of O. U. in a manner similar to their previous work. The final surface was obtained by electropolishing. Six samples numbered one through six were prepared and four of these samples (1 through 4) were irradiated in the Avco/Tulsa radiation facility. The total proton flux on each sample was 10^{17} p/cm² with flux densities of approximately 9×10^{12} p/cm²/sec, at an accelerating energy of 100 Kev.

D. Results

In order to establish that the proton penetration of the aluminum was responsible for the subsequent evolution of hydrogen during heating it was necessary to follow the hydrogen outgassing of the sample heater and virgin (non-irradiated) aluminum samples. It was found that even in a clean, baked-out system, a hydrogen surge was always observed from the empty heater. However, this surge very rapidly dies out, with the hydrogen peak drifting back to equilibrium within 3 to 4 minutes. The peak of this surge occurs before the sample surface temperature

has risen appreciably. Two virgin samples were heated to temperatures as high as 320°C and no significant hydrogen evolution was observed either with the ion pump off or on.

The hydrogen outgassing characteristics of Samples 1 through 4 are shown in Figures 13 through 18. The hydrogen outgassing scale given on Figures 13 through 18 is merely an electrometer scale, however, a comparison of the indicated partial pressures as given by the electrometer scale with the total pressure indicates that the electrometer scale is roughly equivalent to a partial pressure in torr. See Figure 19 in Appendix II. Each of the samples is discussed separately below and the results are summarized in Table I.

TABLE I

Sample	Heating Temp.	Blister	Remarks
1	255°C	Yes	Preheat sample to ~90°C lost much H ₂
2	185°C	No	No blistering
2	255°C	Yes	Reheat of Sample 2 after 185° run
2	305°C	Yes	Reheat of Sample 2 after 255°C run
3	120°C to 235°C	Yes	Step heating without removing from vacuum
4	100°C to 305°C	Yes	Sample sat at 10 ⁻¹⁰ torr, 28°C for 5 days - no H ₂ evolution

Sample 1 - Figure 12. This sample was heated to 255°C and surprisingly little hydrogen evolution relative to other samples was observed. Extensive uniform blistering was noted. Hydrogen gas was evolved, however, over a 7 minute period and seemed to be practically over by the time the sample reached 255°C. Subsequent holding at this temperature evolved

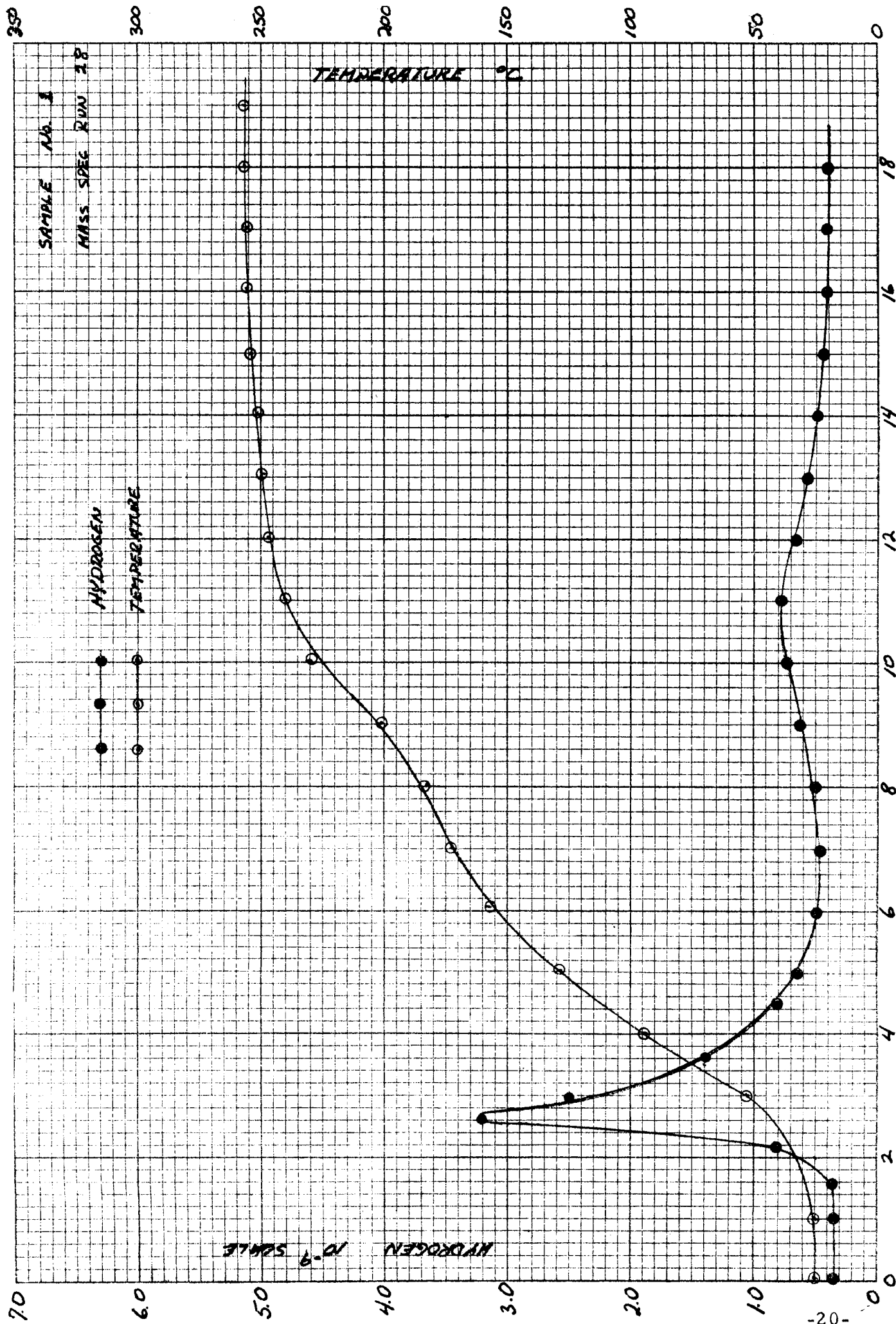


Figure 13 - TIME - MINUTES

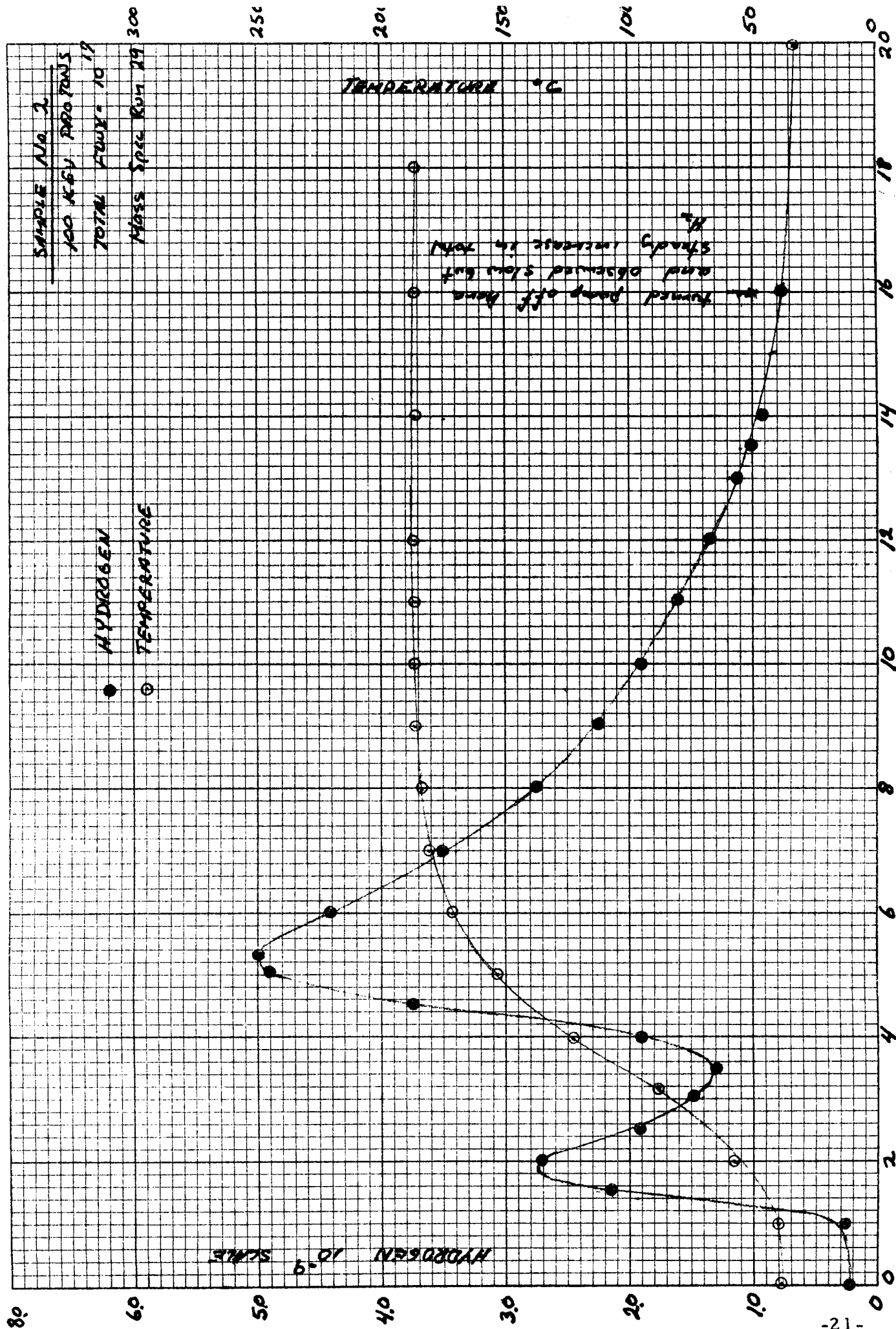


Figure 14 - time - minutes

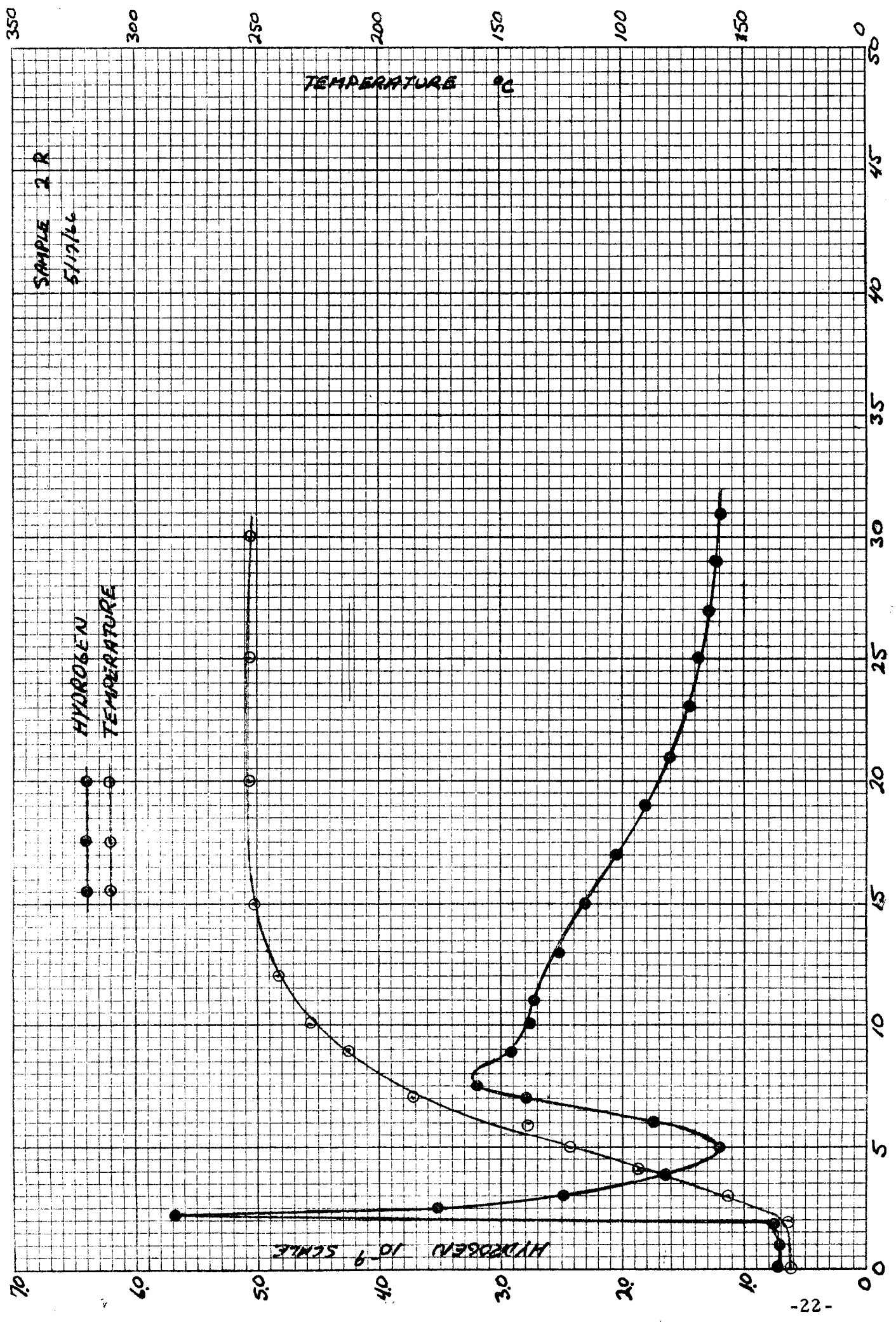


Figure 15

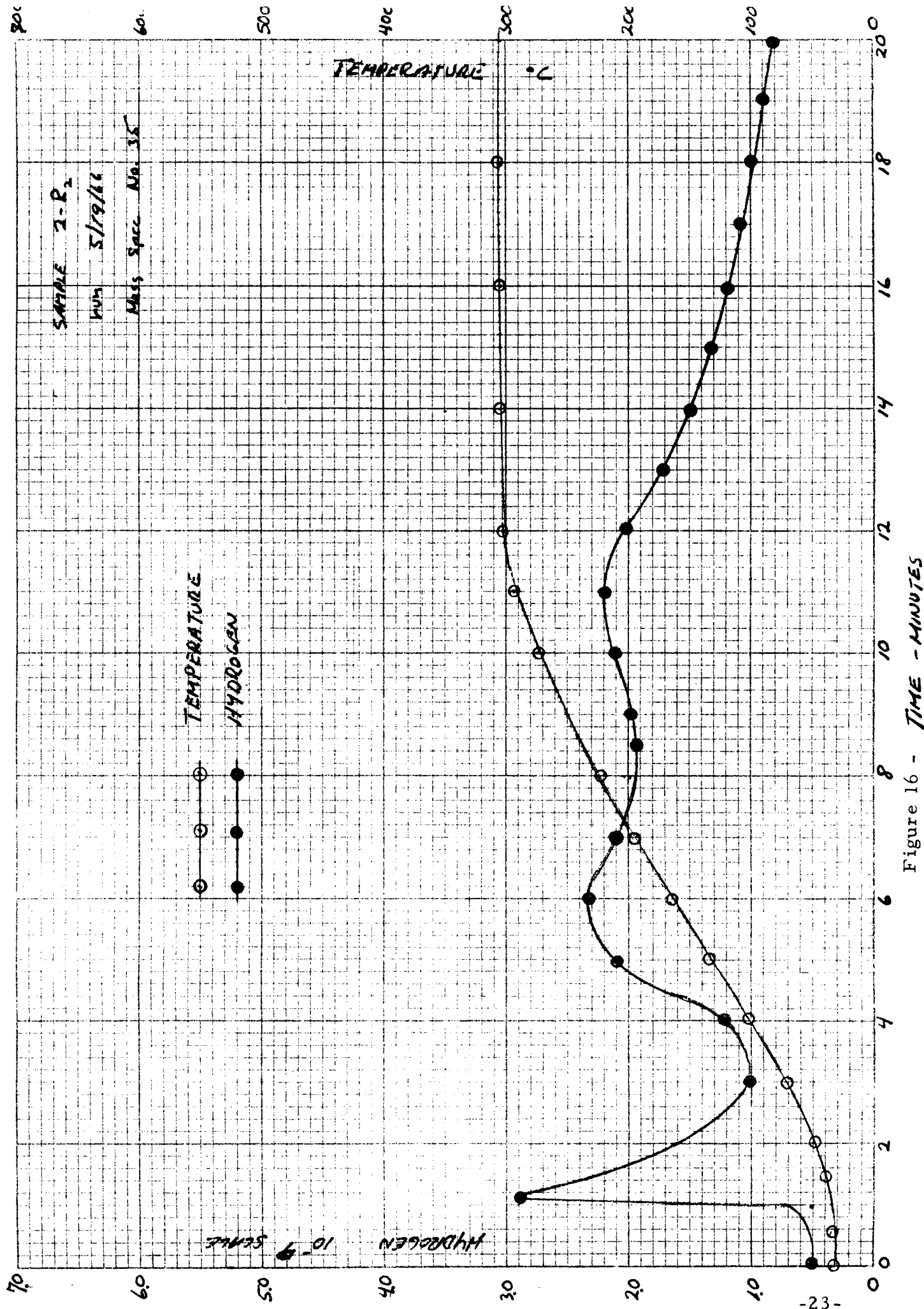


Figure 16 - TIME - MINUTES

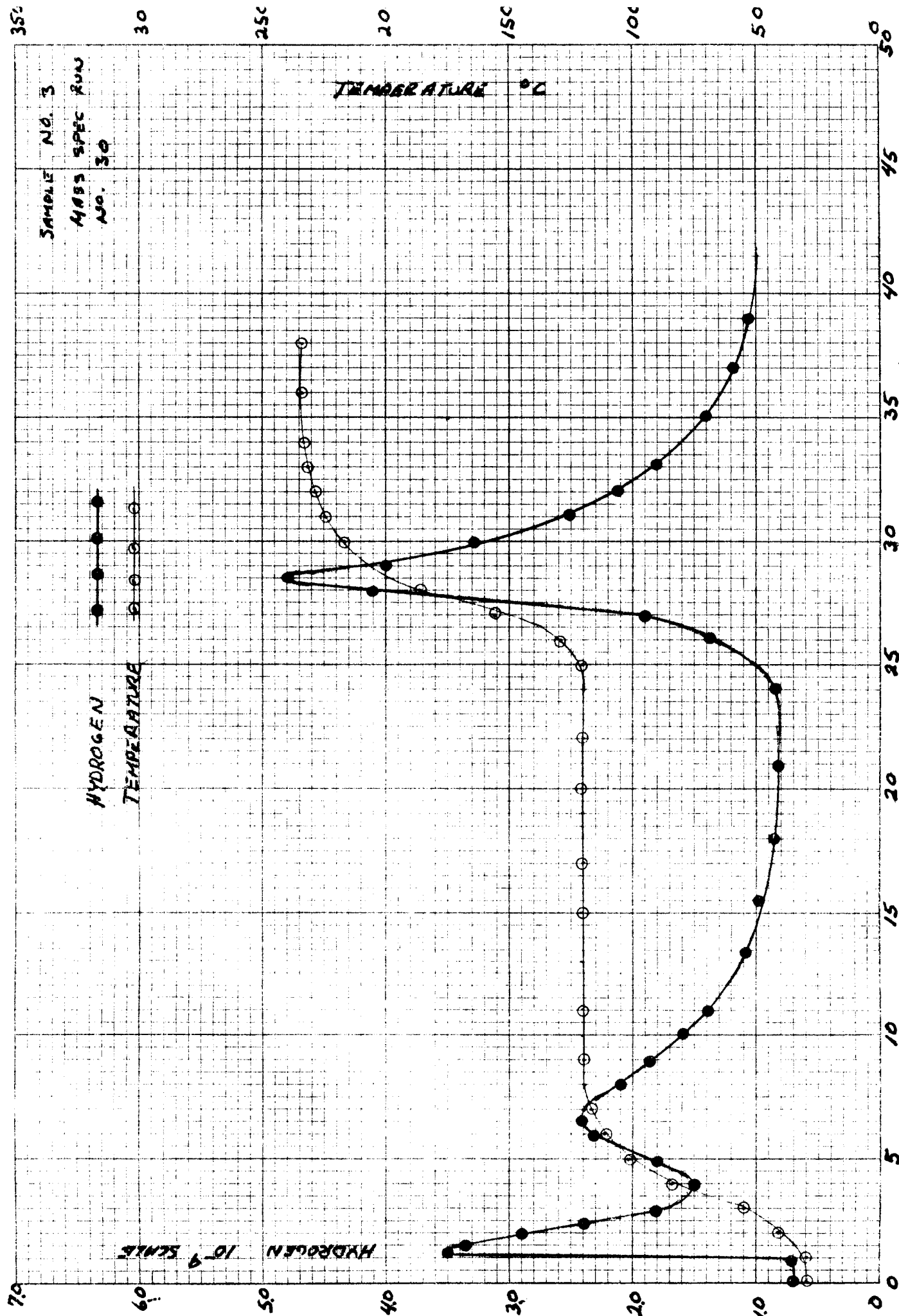


Figure 17 - TIME - MINUTES

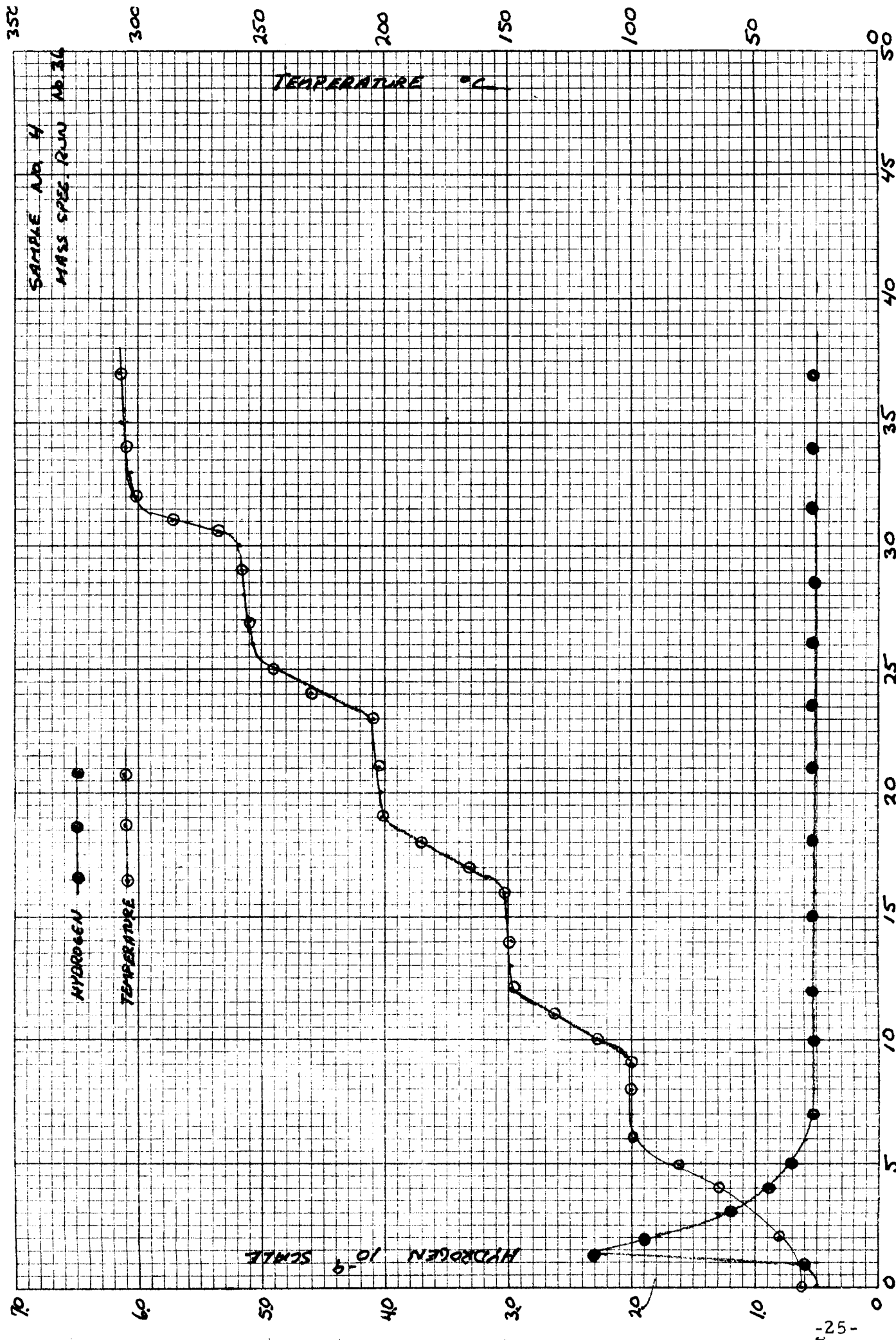


Figure 18 - TIME - MINUTES

no gas. It was later realized that the small amount of hydrogen evolution was probably due to the fact that the system had been baked under vacuum at about 90°C for 4 hours with the sample in the chamber and a considerable amount of hydrogen had already been lost.

Sample 2 - Figures 13, 14, and 15. Sample 2 was first heated to 185°C and considerable hydrogen evolution was noted (Figure 13). The specimen was removed and no blisters were visible under microscopic examination at 500x. The sample was heated again, this time to 255°C and again considerable hydrogen gas was evolved. Microscopic examination revealed that blistering had occurred. The blistering in this case, however, was not entirely uniform as certain areas within the irradiated zone showed no apparent blisters. Sample 2 was reheated once more, this time to 305°C and again hydrogen evolution was noted but in less quantity than previously. The evolution was characterized by a strange double peak that is not understood. The blisters appeared to have the same distribution and density as noted on the previous 255°C anneal but they stood out in much better contrast.

Sample 3 - Figure 16. Sample 3 was first annealed at 120°C until hydrogen evolution was apparently complete and then the temperature was raised to 235°C. Hydrogen evolution was noted again at the higher temperature. Examination of the surface showed uniform blistering but on a slightly finer scale than Sample 1.

Sample 4 - Figure 17. Extreme care was taken with this sample to outgas the sample holder and bakeout the system prior to inserting the sample. The resulting vacuum prior to the heating sequence was 2×10^{-10} torr. Due to various problems, it was not possible to run the sample as soon as the good vacuum was established and the sample remained in the ultra-high vacuum environment at a temperature of approximately 28°C for five days.

The object of this run was to raise the temperature in steps of approximately 50°C allowing the hydrogen evolution to come back to background each time before proceeding to a higher temperature. As can be seen in Figure 17, a small peak

associated with the holder appeared and quickly dropped off and no other outgassing was observed. Microscopic examination of this sample showed that uniform blistering similar to that seen on the other samples was present.

E. Discussion of Results

Hydrogen Evolution

One of the most striking conclusions to be made from the presented data is that the mobility of hydrogen in aluminum is apparently quite high even at low (i. e. ambient) temperatures. This is evidenced by Sample 3 which evolved a considerable amount of H_2 at $120^\circ C$, Sample 1 which lost much of its H_2 due to a $90^\circ C$, 4 hr. bakeout, and Sample 4 which apparently lost all its H_2 at $28^\circ C$ over a period of 5 days in an ultra-high vacuum environment. A crude* estimation of the diffusivity of H_2 subject to several assumptions is given in the appendix and shows that the apparent diffusivity at $120^\circ C$ is approximately $10^{-11} \text{ cm}^2/\text{sec}$.

The hydrogen evolution seems to have a short time and a long time dependence. The short time dependence is evidenced in Samples 2 and 3 where at a given temperature a surge of H_2 is evolved over approximately a ten minute period then upon raising the temperature another similar surge is observed, and, so on to higher temperatures.

The long time dependence is evidenced by Samples 1 and 4 which apparently lost much of their hydrogen at low temperatures ($30 - 100^\circ C$) over long periods of time.

A possible explanation of these observations is that the long time dependence represents the equilibrium situation where H_1 having a very low solubility in aluminum under ultra-high vacuum conditions simply diffuses slowly to the surface and is desorbed as H_2 . The short time H_2 surge phenomenon is probably associated with the temperature dependence of the H distribution. To amplify this idea, we know that the flux (J) of H at any point is given by

$$J = -D \frac{\partial c}{\partial x}$$

*Crude in the sense that the method assumes a distribution model that could be quite in error and the correlating of the H_2 peak with a mathematical flux maxima is open to criticism.

where the terms are defined in Appendix I. As long as the temperature is constant H_2 will diffuse out at a steady rate since we can presume D and the concentration gradient at the surface to be constant. However, if we allow a sudden temperature increase, D is immediately affected, increasing the H_2 loss at the surface. This in turn increases the concentration gradient and a H_2 surge develops. The concentration gradient will, however, re-establish the equilibrium and once again steady loss of H_2 can take place.

The correlation of the H_2 evolution with the appearance or non-appearance of blisters is discussed in the next section. It should be mentioned here, however, that the mass spectrometer could not detect individual blister bursts.

Blistering

There appears to be no correlation between hydrogen evolution and the appearance of blisters. Instead, the appearance of blisters seems to be temperature dependent. An insufficient number of samples were run to establish any time and temperature dependence. No blistering was observed for annealing temperatures as high as 180°C even though relatively large quantities of hydrogen gas were evolved. Annealing of bombarded samples at 230°C and above produced blisters in every instance which includes samples that outgassed relatively large (Sample 2), medium (Sample 3), small (Sample 1) and no (Sample 4) quantities of H_2 gas.

VI. WORK SCHEDULED FOR NEXT PERIOD

The large grain samples of polycrystalline gold which were irradiated in the first quarter will be examined and the results compared to that for aluminum. Aluminum samples will be maintained at high and low temperatures during irradiation to determine the effects of exposure temperature on blister formation.

VII.

APPENDIX IEstimation of the Diffusivity of Hydrogen in Aluminum from Mass Spectrometer Data

We have Fick's first and second laws in the form

$$(1) \quad J = -D \frac{\partial c}{\partial x}$$

where: J = flux

D = diffusion coeff. or diffusivity

$$(2) \quad \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$

c = concentration of diffusing species

x = distance in the diffusion direction

t = time

Thin film solution

The solution to equation (2) for a thin film of solute diffusing in the x direction only in a solute free material of infinite length is:

$$(3) \quad c = \frac{a}{\sqrt{\pi D t}} e^{-(x^2/4Dt)}$$

where a = quantity of solute in the thin film.

Let us now imagine an aluminum single crystal with a planar face that has been subjected to a flux of 10^{17} -100 Kev protons and assume that all the protons are stopped in a band that is thin compared to the penetration distance. The average penetration depth of 100 Kev protons in Al is approximately 10,000 Å according to Wilcox*. The distribution about this depth will be considerably less.

*H. A. Wilcox, Phys. Rev. Vol. 74, No. 12, 1948, p. 1743.

Applying the thin film approximation to this situation, we have after a diffusion anneal at temp "T" and time "t" the distribution

$$(4) \quad c = \frac{a}{\sqrt{\pi Dt}} e^{-(x^2/4Dt)}$$

or

$$(5) \quad c = \frac{A}{t^{1/2}} e^{-(x^2/4Dt)} \quad \text{where } A = \frac{a}{\sqrt{\pi D}}$$

Differentiating (5) we get (with respect to x)

$$(6) \quad \frac{\partial c}{\partial x} = -\frac{2Ax}{4Dt} e^{-(x^2/4Dt)}$$

It is important to find the maximum of this function, therefore,

$$(7) \quad \frac{\partial^2 c}{\partial x^2} = -\frac{2A}{4Dt} \left\{ \frac{-x(2x)e^{-(x^2/4Dt)}}{4Dt} + e^{-(x^2/4Dt)} \right\}$$

Rearranging and equating to zero we get:

$$-\frac{2Ae^{-(x^2/4Dt)}}{4Dt} \left(-\frac{4x^2}{2Dt} + 1 \right) = 0$$

$$\text{or } x^2 = 2Dt$$

equation (6) has a max at:

$$(8) \quad x = \sqrt{2Dt}$$

From equation (1) we know that the flux is proportional to the gradient, i. e.,

$$J = -D \frac{\partial c}{\partial x}$$

therefore, the flux has a maximum given by

$$(9) \quad x = \sqrt{2Dt}$$

This maximum of the flux as a function of time we will equate with the maximum of the hydrogen outgassing (as a function of time).

From mass spec run #30 (-sample No. 3) we observe that the hydrogen peak occurred within 5 minutes from $t = 0$, at 120°C .

Therefore:

$$x = 10,000 \text{ \AA} = 10^{-4} \text{ cm.}$$

$$t = 5 \text{ min} = 300 \text{ sec.}$$

From (9)

$$D = \frac{x^2}{2t} = \frac{10^{-8}}{(2)(300)} = 1.65 \times 10^{-11} \text{ cm}^2/\text{sec} \quad \leftarrow D$$

It seems that the value of D calculated is quite likely a lower bound since the maximum H_2 peak arrived before 120°C was reached and the value of 5 minutes to achieve the peak is an upper bound on the time.

APPENDIX II

VIII.

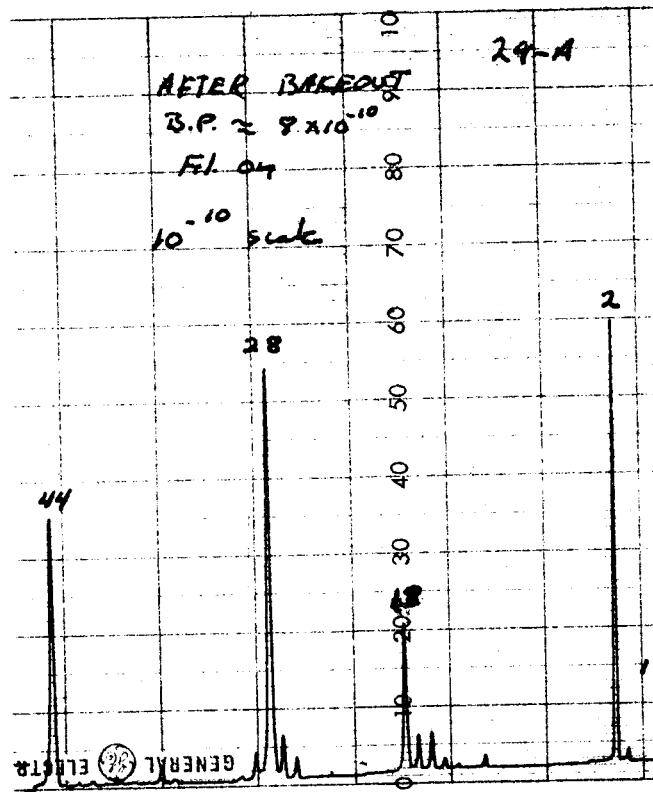


Figure 19 --- Typical mass spec scan from 1 to 50 a.m.u. of chamber gases.